

The University of Chicago

THE ADDITION OF HYDROGEN BROMIDE TO BUTADIENE

A PART OF A DISSERTATION SUBMITTED
TO THE FACULTY OF THE DIVISION OF
THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By
ELLY THOMAS MARGOLIS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE JOURNAL OF ORGANIC CHEMISTRY
Vol. I, No. 4, September, 1936



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41548411_0018

The University of Chicago

THE ADDITION OF HYDROGEN BROMIDE TO BUTADIENE

A PART OF A DISSERTATION SUBMITTED
TO THE FACULTY OF THE DIVISION OF
THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By
ELLY THOMAS MARGOLIS

Private Edition, Distributed by
THE UNIVERSITY OF CHICAGO LIBRARIES
CHICAGO, ILLINOIS

Reprinted from
THE JOURNAL OF ORGANIC CHEMISTRY
Vol. I, No. 4, September, 1936



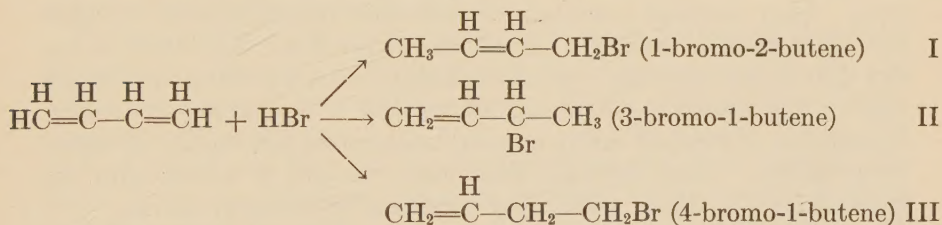
THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS. THE ADDITION OF HYDROGEN BROMIDE TO BUTADIENE*

ELLY THOMAS MARGOLIS

INTRODUCTION

It has been proved that the presence or absence of peroxides in the reaction mixture exercises an important effect on the direction of addition of hydrogen bromide to certain ethylene derivatives.¹ Further study² has shown that this effect appears only when the double bond in question is terminal. These observations have naturally made it necessary to reinvestigate, under rigidly controlled conditions, the addition of hydrogen bromide to conjugated systems. 1,3-Butadiene was selected for study because it is the simplest symmetrical diene, and because *a priori* the difficulties involved in the analysis of the reaction product seemed less formidable for this than for any other conjugated system.

From structural considerations, it is obvious that the addition of one molecule of hydrogen bromide to butadiene may result in any or all of three bromobutenes:



* This work is an abstract, in part, of a dissertation submitted by Elly T. Margolis to the Faculty of the Division of The Physical Sciences of The University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy. A preliminary note appeared in the *J. Soc. Chem. Ind.*, **55**, 663 (1936).

¹ KHARASCH AND CO-WORKERS, *J. Am. Chem. Soc.*, **55**, 2468, 2521, 2531 (1933); **56**, 244, 712, 1212, 1243, 1642, 1782 (1934); **57**, 2463 (1935); **58**, 57 (1936).

² KHARASCH AND M. C. McNAB, *J. Soc. Chem. Ind.*, **54**, 989-990 (1935); KHARASCH AND KLAAS, unpublished work; KHARASCH AND WALKER, unpublished work.

Of these, I (crotyl bromide) should occur in two diameric, and II in two enantiomorphous forms.

The author has found that in the absence of oxygen and peroxides, and in the presence of an antioxidant, butadiene adds hydrogen bromide at low temperatures to give, principally, II by 1,2 addition. At higher temperatures under the influence of hydrogen bromide, and particularly under the combined influence of hydrogen bromide and peroxides, this product rearranges to I. The addition product obtained in the presence of air or added peroxides is principally I (crotyl bromide). Evidence to show whether peroxides cause direct formation of crotyl bromide by 1,4 addition of hydrogen bromide to butadiene, or merely rearrange the 1,2 addition product is lacking. All that can be said with assurance is that in the absence of peroxides 1,4 addition does not occur. A careful but unsuccessful search was made for the third possible addition product, III. Two independent analytical methods indicate that not more than 5 per cent. of this substance could have been present in the reaction products.

PREVIOUS WORK

There is a widespread impression that butadiene adds reagents in the 1,4 positions.³ The addition of bromine to this substance has been studied extensively, and, in view of the fact that the results of the author bear also upon this reaction, it will be discussed in some detail. As early as 1894, Griner⁴ reported that when bromine is added to a chloroform solution of butadiene at -21° , the addition product is 3,4-dibromo-1-butene. He noted also that this compound when heated to 100° rearranges to 1,4-dibromo-2-butene. Farmer, Lawrence, and Thorpe⁵ confirmed Griner's observations. They obtained a mixture of these two dibromobutenes by addition of bromine to butadiene, and they further state that either of the two dibromides rearranges to an equilibrium mixture containing 20 per cent. of 3,4-dibromo-1-butene and 80 per cent. of 1,4-dibromo-2-butene. Equilibrium is attained slowly at room temperature but rapidly at higher temperatures. These findings, they point out, are in accord with the generalization of Gillet,⁶ whom they quote and interpret as follows:

$$\begin{array}{c} \diagup \quad \diagdown \\ C_1 = C_2 - C_3X \\ \diagdown \quad \diagup \end{array}$$

"If in the system $C_1 = C_2 - C_3X$, the total effect of the radicals saturating C_3 is strongly negative in comparison with that of the groups saturating C_1 , the most negative radical attached to C_3 tends to migrate to C_1 If one compares the compound $CH_2=CH-CHBrCH_2Br$ with the examples cited, (examples which follow

³ Cf. THIELE, *Ann.*, **306**, 87 (1899).

⁴ GRINER, *Compt. rend.*, **117**, 553 (1893).

⁵ FARMER, LAWRENCE AND THORPE, *J. Chem. Soc.*, **1928**, 729.

⁶ GILLET, *Bull. soc. chim. Belg.*, **31**, 365 (1922).

the rule) it is found to be in the same category and should very easily undergo, under the influence of traces of acid, the transformation $\text{CH}_2=\text{CH}-\text{CHBr}-\text{CH}_2\text{Br} \rightarrow \text{CH}_2\text{BrCH}=\text{CH}-\text{CH}_2\text{Br}$. Thus in effect two forms are obtained by combining one molecule of bromine with one molecule of butadiene, the second form predominating.' Addition is therefore regarded as taking place at one double bond, the apparent 1:4 addition being sufficiently explained by including the 1:2 dibromide in the category of substances subject to 'negative' migration."

Farmer, Lawrence, and Thorpe point out that the problem is not as simple as Gillet supposed, for the rearrangement is reversible, and the amount of dibromide obtained in some solvents is far more than can be accounted for by rearrangement at the reaction temperature. They also state that the hydrogen bromide which inevitably appears during the bromination of butadiene catalyzes the rearrangement. Careful scrutiny of their paper fails to reveal any unequivocal evidence in support of this statement. By analogy between this addition and that of hydrogen bromide to butadiene, it now seems highly probable that at low temperatures the important catalyst in the rearrangement is not hydrogen bromide alone but hydrogen bromide plus peroxides (oxygen).

The above remarks are equally pertinent to the observations of Prévost⁷ on the addition of bromine to 1,1,4,4-tetramethylbutadiene. He obtained a mixture of liquid and solid dibromides which solidified rapidly; the 1,2 dibromide is a liquid, the 1,4 dibromide a solid.

Several workers have reported on the addition of hydrogen bromide to butadiene⁸, but they were unaware of the easy isomerization of the addition products; hence their work need not be discussed here. Similar objections may be raised to the methods used in the preparation of the bromobutenes from the corresponding alcohols.⁹

The present investigation was greatly facilitated by the work of Young and Winstein.¹⁰ These investigators showed that 3-bromo-1-butene (II) and 1-bromo-2-butene (I) are partially interconvertible. Each yields an equilibrium mixture containing 15 per cent. of II and 85 per cent. of I. The data of Young and Winstein, besides furnishing important physical constants of the two bromides, show the necessity for the low-temperature technique which the author had already adopted in the distillation of the mixture formed by the addition of hydrogen bromide to butadiene.

ADDITION OF HYDROGEN BROMIDE TO BUTADIENE

The technique and precautions necessary to obtain the results here recorded and the constants needed for the analysis of the reaction products

⁷ PRÉVOST, *Compt. rend.*, **184**, 1460 (1927).

⁸ IPATIEW, *J. prakt. Chem.*, [2], **67**, 420 (1903); *D. R. P.*, 522, 650.

⁹ CHARON, *Ann. chim. phys.*, **7**, 17, 232 (1899); BAUDRENGHIEN, *Bull. soc. chim. Belg.*, **31**, 160 (1922); GREY AND PIAUX, *Bull. soc. chim.*, [5], **1**, 1481 (1934).

¹⁰ YOUNG AND WINSTEIN, *J. Am. Chem. Soc.*, **57**, 2013 (1935); **58**, 104 (1936).

are described in the experimental part. Data supporting the claim that no appreciable quantities of 4-bromo-1-butene (III) appear in the reaction products are also given there.

Table I shows the results obtained when hydrogen bromide is added to butadiene *in vacuo* and in the presence of antioxidants. At -78° about 80 per cent. of the product is 3-bromo-1-butene (II). Around 0° , the yield

TABLE I
ADDITION OF HYDROGEN BROMIDE TO BUTADIENE IN VACUO AND IN THE PRESENCE OF ANTIOXIDANTS

ANTIOXIDANT ^a	REACTION		YIELD ^b BROMO- BUTENES (%)	COMPOSITION OF BROMOBUTENE MIXTURE			
	Temp. (°C.)	Time (hours)		(By n_D^{23})		(By d_4^{25})	
				1-Br-2- butene (%)	3-Br-1- butene (%)	1-Br-2- butene (%)	3-Br-1- butene (%)
Diphenylamine ^c	-78	1	65	10	90		
Diphenylamine ^c	-78	2	76	10	90		
Diphenylamine.....	-78	3	82	19	81	10	90
Hydroquinone.....	-78	18	89	18	82	14	86
Diphenylamine.....	-12	1.5	78	28	72	18	82
	-78	15					
Diphenylamine.....	-12	2	85	25	75	18	82
Thiophenol ^d	-12	4	92	31	69	26	74
Thiophenol.....	-12	4	90	21	79	20	80
Diphenylamine ^e	-12	4	>70	35	65	35	65
Diphenylamine ^e	-12	4	>80	31	69		
Diphenylamine.....	0	1.5	90	38	62	36	64
Diphenylamine.....	0	1.5	93	29	71	29	71
Diphenylamine.....	room	1.5	92	56	44	54	46

^a Quantities given in experimental part.

^b On initial butadiene, after first distillation to remove free hydrogen bromide and part of unchanged butadiene.

^c Distilled only once before analysis by index of refraction.

^d Distilled three times before analysis by index of refraction.

^e Hydrogen bromide added very slowly in special apparatus described in experimental part.

of this product decreases to 60-70 per cent.; at room temperature still less is obtained. These results indicate that the primary product of the uncatalyzed reaction is 3-bromo-1-butene (II, formed by 1,2 addition), and that under the experimental conditions, the amount of rearrangement of this bromide to 1-bromo-2-butene (I) depends either upon the temperature, or, more probably, upon the increased activity at higher temperatures of minute amounts of peroxides present in butadiene.

Table II shows that more 1-bromo-2-butene (I) is obtained under corresponding conditions (*cf.* Table I) in the presence of air or when the anti-oxidant is replaced by an "added" peroxide. At -78° , about 40 per cent., at -15° , about 70–80 per cent., of I is obtained. As in the case of the antioxidant experiments *in vacuo*, the proportion of 1-bromo-2-butene increases with temperature, but we are unable to state the precise cause of

TABLE II

ADDITION OF HYDROGEN BROMIDE TO BUTADIENE IN THE PRESENCE OF AIR AND PEROXIDES

PEROXIDE ^a	REACTION		YIELD ^b BROMO- BUTENES (%)	COMPOSITION OF BROMOBUTENE MIXTURE			
	Temp. (°C.)	Time (hours)		(By n_D^{23})		(By d_4^{25})	
				1-Br-2- butene (%)	3-Br-1- butene (%)	1-Br-2- butene (%)	3-Br-1- butene (%)
Ascaridole ^c	-78	1	71	41	59		
Ascaridole ^c	-78	2	96	44	56		
Ascaridole.....	-12	2	93	78	22	74	26
Benzoyl peroxide.....	-12	3.5	85	77	23	71	29
Ascaridole.....	-12	3		81	19		
None.....	-12	3.5	82	73	27	62	38

a, b, c Have the same significance as in Table I.

TABLE III

EFFECT OF HYDROGEN BROMIDE AND PEROXIDES ON MIXTURES OF
1-BROMO-2-BUTENE AND 3-BROMO-1-BUTENE.

ADDENDA	TEMP.	TIME	n_D^{23} INITIAL	n_D^{23} FINAL	CONCLUSIONS
Ascaridole.....	-12°	4 hr.	1.4666	1.4666	No effect
Ascaridole and HBr...	-12°	4 hr.	1.4666	1.4778	Converted to equilibrium mixture
HBr alone.....	-12°	4 hr.	1.4644	1.4666	Slight effect
HBr alone.....	30–45°	5 min.	1.4671	1.4771	Converted to equilibrium mixture

this change. It may be due either to a direct or an indirect effect. That is, the peroxide may produce a 1,4 instead of a 1,2 addition, or it may catalyze the isomerization of the 1,2-addition product first formed. More crotyl bromide than corresponds to the equilibrium mixture (85 ± 5 per cent.) was not found in any experiment.

Table III shows the remarkable effect of hydrogen bromide and peroxides in rearranging 3-bromo-1-butene (more correctly a mixture of 70

per cent. of II and 30 per cent. of I) to the equilibrium mixture (15 per cent. II and 85 per cent. I).

Thus, at -12° ascaridole alone has no effect on the rearrangement; hydrogen bromide alone has a slight effect; but the two reagents together cause rapid isomerization. No undue importance should be attached to the time interval of four hours, for equilibrium by isomerization may have been attained in less time. The action of hydrogen bromide at $30-45^{\circ}$ may be an effect *per se*; more probably what is observed is the combined isomerizing effect of hydrogen bromide plus minute, yet significant, quantities of peroxides. This latter suggestion is in harmony with all available knowledge of the relationship between temperature and peroxide (oxygen) effect.

The rate of introduction of hydrogen bromide into butadiene is of minor importance. Table I shows that when hydrogen bromide was added to butadiene very slowly (3-4 hours) so as to retard the addition reaction the results were the same as when theoretical quantities of butadiene and hydrogen bromide were brought to the reaction temperature in a few minutes. The addition of hydrogen bromide to butadiene, in contrast to some other unsaturated compounds, is very rapid (almost instantaneous) even at low temperatures.

ADDITION OF HYDROGEN BROMIDE TO 1-BROMO-2-BUTENE AND 3-BROMO-1-BUTENE

The two products of the addition of one mole of hydrogen bromide to butadiene may add a second mole of hydrogen bromide as follows:

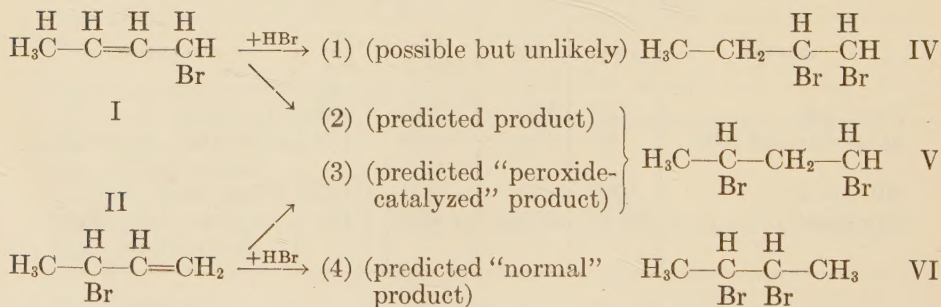


Table IV shows the results of the addition of hydrogen bromide to both 1-bromo-2-butene and 3-bromo-1-butene in the presence of peroxides or antioxidants. The mixtures were analyzed by index of refraction and also by distillation through a modified Podbielniak column¹¹ at 50 mm. pressure. Good separations were obtained, and the two methods of analysis

¹¹ PODBIELNIAK, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

checked satisfactorily. The products from either bromobutene, under both sets of conditions, were mixtures of 1,3- and 2,3-dibromobutanes (V and VI). There was no indication of the presence of any 1,2-dibromobutane (IV).

The experimental results of Table IV confirm previous observations that substances which contain nonterminal double bonds give the same addition product either in the presence or the absence of peroxides. Thus, 1-bromo-2-butene (I) gives about 80 per cent. of the predicted product, 1,3-dibromobutane (V), irrespective of the experimental conditions. But hydrogen bromide accelerates the attainment of equilibrium between I and II; hence the 20 per cent. of VI found in the reaction mixture probably

TABLE IV

ADDITION OF HYDROGEN BROMIDE TO 1-BROMO-2-BUTENE AND 3-BROMO-1-BUTENE

BROMIDE	PEROXIDE OR ANTIOXIDANT	MOLES ^a	BY η_D^{20}		BY FRACTIONAL DISTILLATION		REACTION		YIELD (%)
			% 2, 3	% 1, 3	% 2, 3	% 1, 3	Time	Temp.	
1-Br-2-butene	Ascaridole	.077	20-0	80-100	22 ^b	78	2 days	0°	60
1-Br-2-butene	Diphenylamine	.076	13	87			2 days	0°	
1-Br-2-butene	Ascaridole	.075	17	83			1½ days	Room	88
1-Br-2-butene	Diphenylamine	.077	13	87			4 days	Room	94
3-Br-1-butene	Diphenylamine	.062	53	47	62	38	3½ days	Room	82
3-Br-1-butene	Ascaridole	.070	17	83	25	75	3½ days	Room	95

^a Moles peroxide or antioxidant per mole of bromobutene.

^b Since these addition products had the same boiling ranges on preliminary distillation and approximately the same indices of refraction, they were distilled together.

^c Yield actually obtained, not allowing for loss in accident. Estimated yield 80-95 per cent.

comes from the normal addition of HBr to II. The addition of hydrogen bromide to 3-bromo-1-butene in the presence of added peroxide gives the same mixture (80 per cent. V and 20 per cent. VI). The fact that, upon addition of hydrogen bromide, 3-bromo-1-butene, in the presence of peroxides, and 1-bromo-2-butene, under all conditions, give the same reaction mixture, is to be expected in view of the rapidity with which equilibrium is established between the two bromobutenes under "peroxide" conditions. In the absence of air and peroxides, however, 3-bromo-1-butene (II) gives mostly (60 per cent.) 2,3-dibromobutane (VI). The formation of such a large quantity of 2,3-dibromobutane is most striking because the addition was carried out at room temperature, *i.e.* under conditions which cause exceedingly rapid rearrangement of the 3-bromo-1-butene to

1-bromo-2-butene in the presence of minute amounts of peroxides. Our samples of 3-bromo-1-butene were, therefore, quite free of peroxides and, furthermore, considerable addition must have taken place before the equilibrium between the two bromobutenes was established.

These results on the addition of hydrogen bromide to the two bromobutenes, under peroxide and antioxidant conditions, are in complete agreement with the thesis, developed on the basis of the addition of hydrogen bromide to butadiene, that the rearrangement of 3-bromo-1-butene (II) to 1-bromo-2-butene (I) (crotyl bromide) is due to a combined effect of hydrogen bromide and peroxide (and/or oxygen). For emphasis it is repeated that the observed effect of temperature on this rearrangement is due to increased activity with increasing temperature of minute quantities of peroxides (and/or oxygen) in the reaction mixture. Furthermore, because of the rearrangement of 3-bromo-1-butene to 1-bromo-2-butene under the influence of peroxides, it is impossible to conclude from the present data whether in the presence of peroxides V is formed from II by reaction (3) or from I by reaction (2). Whatever the mechanism, however, peroxides play an important part in the addition.

EXPERIMENTAL

*Preparation of Butadiene.*¹²—Cyclohexene was placed in a 500-cc. round-bottomed flask on a hot-plate. From the flask, cyclohexene vapor passed up into a tube containing a spiral made of four feet of #24 platinum wire, maintained at a bright red heat. Atop this tube was a condenser to reflux back unchanged cyclohexene. The effluent vapors were passed through a trap in an ice bath to remove any cyclohexene passing through the condenser, and condensed in a second trap at -78° . From this trap the crude butadiene was distilled into a solution of bromine in carbon tetrachloride until the solution was colorless. This mixture, on standing several hours in the refrigerator, yielded crystalline material. The crystals were collected on a filter, washed with small portions of carbon tetrachloride and crystallized three times from alcohol; m.p. 117° . Medium-boiling ligroin (60°) can also be used as a solvent.

To regenerate the butadiene, the purified tetrabromide was put in the thimble of a large Soxhlet extractor fitted to a one-liter round-bottomed flask containing zinc and alcohol. To the Soxhlet was fitted a large double-jacketed condenser to which was sealed a Kjeldahl bulb to protect the scrubbing train in case the condenser flooded. From the condenser the butadiene passed down through a long tower of calcium chloride, and final traces of alcohol were removed by passing the gas through a U-tube of calcium chloride maintained at 0° . It was then trapped at -78° . Butadiene was drawn from the trap as required.

The addition of hydrogen bromide to butadiene under antioxidant conditions: Method 1.—The technique was essentially that described by Kharasch and Mayo,¹ modified because of the very rapid reaction of hydrogen bromide and butadiene even at low temperature. A tube of convenient length was fitted with a two-hole stopper

¹² KISTIAKOWSKY *et. al.*, *J. Am. Chem. Soc.*, **58**, 146 (1936).

carrying a delivery tube and a calcium chloride tube. The tube was then immersed in an acetone-carbon dioxide bath, and the requisite amount of butadiene, 6–10 g., was distilled in. Phosphorus pentoxide was added and a glass-wool plug was inserted. One equivalent of hydrogen bromide per mol of butadiene was condensed, using the same procedure (save that liquid nitrogen was necessary as the refrigerant). Phosphorus pentoxide was added and a glass-wool plug was inserted. The two tubes were strongly cooled and sealed to the yoke. In the third tube was placed 0.3 g. of antioxidant. After reducing the pressure to the limit of a three-stage mercury-vapor pump, the system was sealed off from the vacuum line, the tube containing the antioxidant was cooled in liquid nitrogen and the contents of the other two were allowed to thaw. After distillation was complete the reaction tube was sealed off and plunged into a bath at the desired temperature.

Method 2.—Runs wherein the hydrogen bromide was to be added slowly were carried out in the apparatus illustrated in Fig. 1. The antioxidant was inserted through opening *C*. A plug was then put in opening *A*, a calcium chloride tube was attached at *C*, and the desired amount of butadiene was distilled in through *B*. *C* was then sealed off, the vessel was sealed to the vacuum line at *A*, and the side-arm was sealed on at *B*. The requisite amount of hydrogen bromide was condensed in a long, narrow (16 mm.) tube, and phosphorus pentoxide and a glass-wool plug were put in. The tube was sealed to the reaction vessel as indicated in the diagram. The system was then evacuated and sealed off at *A* and *D*. It was found that when the reaction vessel was kept at -12° in an ice-salt bath, hydrogen bromide would bubble in at a suitable rate from an acetone-carbon dioxide bath. By raising and lowering the Dewar about the hydrogen bromide tube the rate of passage of the hydrogen bromide could be regulated so as to take 3 to 4 hours for completion; the rate could be followed by means of a marker on the hydrogen bromide tube.

When the hydrogen bromide had all passed over, the reaction vessel was cooled and sealed off at *B*.

The addition of hydrogen bromide to butadiene under peroxide conditions.—The butadiene was drawn as described under method 1 in the previous section, and 0.5 g. of a peroxide was then weighed into the tube. Because of the fairly high vapor pressure of butadiene at ice-salt bath temperatures, the tube was immersed in the bath for a period before weighing. Hydrogen bromide was then passed in until the calculated gain in weight had taken place and the tube was then sealed.

The treatment of the reaction products.—At the desired time the end of the reaction tube was cooled to -78° and the tip was broken off; a delivery tube into which a Kjeldahl bulb was incorporated was then sealed on. The delivery tube led into a receiver into which had been weighed one gram of anhydrous potassium carbonate for the purpose of removing unreacted hydrogen bromide and traces of water. The receiver used was a test-tube which had a side-arm sealed on near the top. The receiver was immersed in an acetone-carbon dioxide bath and attached in some instances to a water pump, in others to an oil pump. In the former cases the tube containing the reaction product was warmed to 50 – 60° ; in the latter, distillation was carried out at room temperature. When, however, the low pressure distillation was eliminated, the product, regardless of experimental conditions, assayed 82 per cent of crotyl bromide by refractive index, 84 per cent of this substance calculated from the density. The logical explanation for this, confirmed by Table IV, is that at the higher temperature of the distillation the combined effects of small amounts of peroxides and free hydrogen bromide cause rearrangement. The product was then shaken with potassium carbonate until no fumes could be detected, and filtered into a distilling apparatus consisting of a modified Claisen flask of about

15 cc. capacity, with a relatively long side-neck indented in the manner of a Vigreux column; to this was sealed a small water condenser terminating in a delivery tube which reached well down into the receiver. The receiver was immersed in an ice bath, and distillation was interrupted while the receivers were changed. The pressure was maintained at 93 mm. by means of a constant pressure regulator. Experiments showed that in the absence of hydrogen bromide, rearrangement did not take place during this distillation.

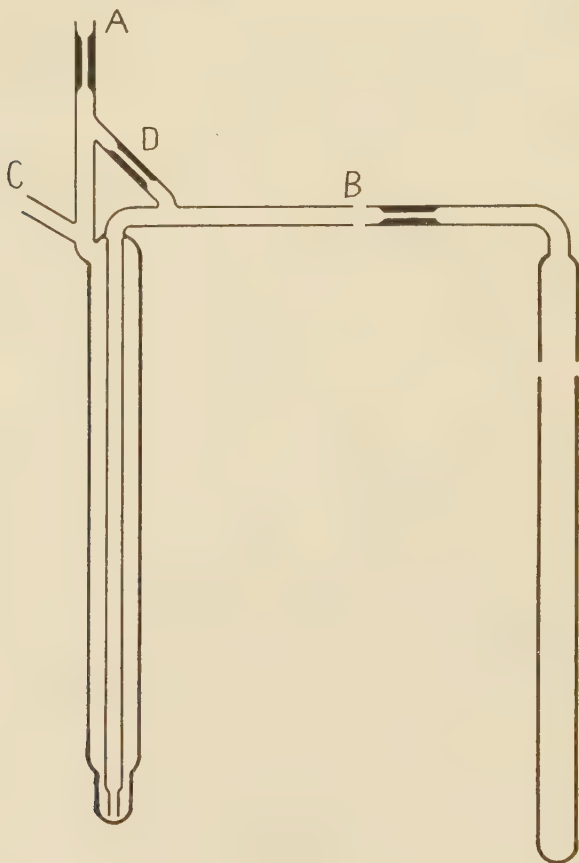


FIG. 1

The addition of hydrogen bromide to bromobutene.—Ten grams of the bromobutene was weighed into a tube, the tube was cooled to -78° , and 1.5 to 2 moles of hydrogen bromide was passed in in the manner described by Kharasch and Mayo.¹ For a peroxide run ascaridole was added, and the tube was sealed; in the case of an anti-oxidant run phosphorus pentoxide was added, and the tube was sealed to a yoke in the manner described by Kharasch and Mayo. The bombs were allowed to stand four days at room temperature, cooled, opened, and after the major portion of the excess hydrogen bromide had escaped, distilled at 50 mm. The distillate in the

case of the peroxide runs was shaken with concentrated sulfuric acid to remove possible ascaridole decomposition products, washed with water, dried with calcium chloride and distilled at 50 mm.; the sulfuric acid wash was omitted in working up the antioxidant runs. The yield was about 90 per cent. In each case the first 3-5 per cent of the final distillate was rejected. This may make our estimate of composition as much as 5 per cent low in 2,3-dibromobutane.

Physical constants and methods of analysis of the bromobutenes.—The papers of Young and Winstein¹⁰ provided the constants shown in Table V, and showed that the indices of refraction of mixtures vary linearly with composition. At the conclusion of the present work on the addition of hydrogen bromide to butadiene, the addition products were combined and fractionally distilled at 10 mm. pressure through a mod-

TABLE V
PHYSICAL CONSTANTS OF BROMOBUTENES

	B.P./10 MM.	n_D^{20}	n_D^{25}	n_D^{35}	d_4^{25}
1-Bromo-2-butene (K., M., M.)	13°	1.4822	1.4805	1.4794	1.3371
Young and Winstein			1.4805	1.4795	1.3335
3-Bromo-1-butene (K., M., M.)	7°	1.4618	1.4608	1.4599	1.2998
Young and Winstein			1.4612	1.4602	1.2998

TABLE VI
PHYSICAL CONSTANTS OF SOME DIBROMOBUTANES

DIBROMOBUTANES	B.P./50 MM.		n_D^{20}	
	Expt.	Recorded	Expt.	Recorded
2,3-Dibromobutanes ¹³	meso 71-4° rac.	72.7-72.9° 75.6-75.8°	1.5123	1.5116 1.5147
1,2-Dibromobutane ¹³		80.5-80.7°		1.5150
1,3-Dibromobutane	88°	89.5° ¹⁴	1.5093	1.507 ¹⁵

ified Podbielniak column.¹¹ Pure samples of 3-bromo-1-butene and 1-bromo-2-butene were thus obtained and the supply of the former was amplified by distillation of the latter at atmospheric pressure and redistillation at 10 mm. No indication of any other bromobutene was found. The author redetermined the constants of Young and Winstein with these pure samples, using a Bausch and Lomb Abbé refractometer and a 3-cc. Ostwald pycnometer. These density determinations were made with smaller samples than they used, and are not corrected to vacuum, but the author checked all values and finds that the composition of a mixture obtained from a density measurement agrees better with that obtained from index of refraction when his constants are used. The author's constants appear in Table V together with those of Young and

¹³ DILLON, YOUNG, AND LUCAS, *J. Am. Chem. Soc.*, **52**, 1953 (1930).

¹⁴ FARGHER AND PERKIN, *J. Chem. Soc.*, **105**, 1356 (1914).

¹⁵ PARISELLE, *Ann. chim. phys.*, [8], **24**, 332 (1911).

Winstein. The density of 3-bromo-1-butene is estimated (but with considerable precision) because it isomerized so rapidly. Thus the index of refraction of a sample was found to increase by .0003 during a density determination.

According to Newman and Rydon¹⁶ either 1-bromo-2-butene or 3-bromo-1-butene hydrolyzes to the extent of 70 per cent in 24 hours at room temperature in 50 per cent. acetone while 4-bromo-1-butene is not attacked. The addition products of the author showed a uniform hydrolysis of 96 per cent. under the same conditions. The author takes this to indicate the absence of appreciable quantities of 4-bromo-1-butene in our addition products, in confirmation of the fractional distillation already referred to. The author is unable to account at this time for the discrepancy in the rates of hydrolysis reported by Newman and Rydon and those observed by him.

Physical constants and methods of analysis of the dibromobutanes.—Fractional distillation of the dibromobutanes obtained from the addition of hydrogen bromide to the bromobutenes gave good separations of the 2,3- and 1,3-dibromobutanes, with no indication of the presence of 1,2-dibromobutane. The physical constants noted are compared with the recorded values in Table VI.

The data indicate that the 2,3-dibromobutane obtained was a mixture of the meso and racemic forms. Compositions of addition products based on indices of refraction in Table IV assume that the index of refraction is a linear function of composition.

SUMMARY

1. In the presence of antioxidants and in the absence of air, hydrogen bromide adds to butadiene to give mostly the 1,2-addition product, namely, 3-bromo-1-butene. In the presence of air (or peroxides) the major product is 1-bromo-2-butene, corresponding to 1,4 addition.

2. Hydrogen bromide in the presence of oxygen or peroxides, has a pronounced catalytic effect on the isomerization of 3-bromo-1-butene to an equilibrium mixture containing 80–85 per cent. 1-bromo-2-butene.

3. The addition of hydrogen bromide to 1-bromo-2-butene (a substance which does not contain a terminal double bond) in the presence of either antioxidants or peroxides, yields the same mixture of 1,3- and 2,3-dibromobutanes.

4. The addition of hydrogen bromide to 3-bromo-1-butene in the presence of air and peroxides gives 80 per cent. of 1,3-dibromobutane and 20 per cent. of 2,3-dibromobutane, while under antioxidant conditions 60 per cent. of the 2,3-dibromobutane is formed.

5. A consistent adequate explanation, based upon the effect of oxygen (or peroxides) in the isomerization of the bromobutenes, is developed to account for the observed results.

6. It has been definitely shown that the apparent 1,4 addition of hydrogen bromide to butadiene at low temperatures is due to an oxygen (or peroxide) effect.

7. It is suggested that the 1,4 addition of bromine to butadiene proceeds through the formation of the 1,2 addition product (as assumed by many) and that the rearrangement is catalyzed by hydrogen bromide and peroxides.

¹⁶ NEWMAN AND RYDON, *J. Chem. Soc.*, **1936**, 261.

